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on

Lead and its Preparations

by

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Of

Lead and its Preparations

This metal seems to have been known in the earliest ages; the mines of Derbyshire it is supposed were wrought in the time of the Romans, the proofs of which are derived from blocks of lead which were found with Roman inscriptions upon them: a pig of lead of this kind was discovered on Cromford moor in the year 1777 and the interpretation of the inscription which has been given is the following "The sixth legion inscribe this in memory of the Emperor Adrian. Another block of lead was met with at Matlock bank in 1783, this also had upon it an inscription signifying that it had been the property of Lucius Aruconius Verecundus, a merchant of London: the weight of this block is 84 pounds. It is also often mentioned by Moses and is described by Homer, as being in common use at the period of the Trojan war.—

The ore now exists in great abundance and under a great variety of forms and combinations, in many parts of the world.—

It is most commonly met with in the state of sulphuret; the carbonate and phosphate of lead are not rare, but the Chromate, Molybdate and sulphate of lead are more uncommon.

The sulphuret of lead, or as it is commonly termed galena, is that combination from which the metallick lead in quantity is obtained. the proceſs it generally undergoes is very simple: the ore is roasted in a furnace untill the greater part of the sulphur is driven off; after this is effected, on increasing the heat, the metal separates from the scoria and settles at the bottom of the furnace. But lead when thus procured is frequently impure, it may be alloyed with other metals, as for instance Iron, Tin, Zinc, or Copper: to free it from these and render its purity perfect, it may be diſsolved in nitric acid, precipitated with sulphate of soda, and after being well washed, the precipitate is reduced by fusing it with three times its weight of black flux in a crucible.—

Lead, is of a dull white or greyish colour, having a blue tinge and considerable brilliancy, but soon tarnishes on being exposed to the air; when rubbed by the finger it emits a peculiar odour; applied to the tongue it has at first scarcely any taste, but leaves a disagreeable

impreſsion; it is very soft and flexible, but poſseſses leſs tenacity than any other metal, a wire 1/10 of an inch in diameter, will break with a weight of thirty pounds: it is also the least sonorous of all the metals, giving when struck a flat heavy sound. Owing to its poſseſsing so little tenacity, it is incapable of being drawn into a fine wire; though it may be extended into thin plates under the hammer; its specific gravity is 11·352, being rather greater than that of silver.—

Authors differ in their statements, with regard to the degree of heat which lead requires for its fusion; Thomson in his system of chemistry mentions it, according to the experiments of Mr Crichton of Glasgow as being at the temperature of 612° Fht; Brande, says 600°, Dr Millar in his elements of chemistry published at Edenburg in 1820, mentions it as being according to some authors 594, though he himself speaks of it as fusing at the 540th degree of Fahrenheit.—

But I would enquire, how can this difference of opinion be accounted for? If it could be supposed that the lead fused by these experimenters was impure, then a very plausible reason for the difference might be given. Suppose for instance the lead which Dr Millar speaks of as fusing at the 540th degree, should have contained a small

portions of tin, (the fusing point of which indicates 442) this certainly would have made a material difference; for notwithstanding the superior degree of heat which it requires for fusion, it is known that two parts of lead and one of tin form an alloy, more fusible than either metal alone*

From this fact it would appear probable, that the admixture of a much smaller portion of tin, than the proportion forming solder would decrease sufficiently the degree of heat required to fuse it, to account for the differences existing.—

Lead is brittle at the time of congelation. In this state it may be broken to pieces with a hammer and the crystallization of its internal parts, will exhibit an arrangement of parallel lines.—

When lead is melted in the open air, [illegible] an [illegible] pellicle forms on the surface which gradually changes to a uniform grey colour. When this pellicle is removed another forms and in this way the whole lead may be converted into this substance. If these pellicles be heated and agitated for a short time in an open vessel, they assume the appearance of a greenish yellow powder; this colour as Mr Proust has shown is supposed to be derived from a mixture of yellow oxide and a portion of lead

in the metallic state. —

If we continue to expose this powder to a heat for sometime longer in an open veſsel, it absorbs more oxygen, aſsumes a yellow colour, and is then known in commerce by the name of maſsicot. This change is owing to the absorption of oxygen by the metallic portion of the droſs, converting the whole into a homogeneous compound.

This oxide, by being subjected to strong heat in a furnace for from about 50 to 60 hours is converted into a red powder now known in the arts by the name of minium or red lead: this is the highest state of oxygenation which can be effected by mere calcination; but there is yet another oxide called the brown, puce, or flea colour; this is obtained by pouring nitric acid of the specific gravity 1.260 upon red lead; 185 parts of the oxide are diſsolved, being in the state of a yellow and the remainder is formed into this brown oxide. The theory advanced by S H Davy is, that the oxide which diſsolves during its solution, on forming maſsicot affords oxygen to the undiſsolved portion, so as to convert it into the new substance. —

This oxide may be procured also by passing a current of oxymuriatic acid or chlorine gas, through water in which the red oxide is kept suspended, and by precipitating it with caustic potash —

From what has been said lead appears capable of combining with oxygen in different proportions, and three of its combinations with this substance appear to be ..... these are distinct oxides; the two containing the lesser proportion of oxygen may be formed by heat with the access of air; these when thus prepared constitute massicot and minium. The third which contains the greatest proportion of oxygen requires the action of an acid, and from the quantity of oxygen contained in its composition has received the name of per oxide. — These substances were carefully investigated by Berzelius, and according to his statements are composed of oxygen and metal in the proportions — as follows

The first or massicot appears to be composed of

Lead	92.85	100.	1298.7
Oxygen	7.15	7.7	1000.

The second or minium, appears to consist of

Lead	90	100
Oxygen	10	11.08

The third or per oxide Berzelius found to consist of —

Lead	86.51	100.
Oxygen	13.49	15.6

In comparing the proportions of oxygen united with 100 parts of lead in these three oxides, we

shall find the numbers 7.7, 11.55 and 15.4 are nearly in the proportion of 1, 1½ and 2, If therefore we multiply these last numbers by 2 we shall have the oxygen of the three oxides of lead represented by 2, 3, 4 and this view of the subject would render it probable that there exists an oxide of lead, with less oxygen than any at present known. The yellow oxide of lead when precipitated by pure alkalies from its compounds forms a white hydrate the composition of which is not exactly known. —

The oxides of lead are easily vitrified, and have the property of uniting with all the metals, excepting gold and silver. Hence gold or silver may be purified by melting them with lead.

The oxides also give up their oxygen on the application of heat. When distilled in an earthen retort they afford oxygen gas; and still more readily when distilled with concentrated sulphuric acid.

The oxides of lead are also reduced by being ignited with combustible matter: thus when a mixture of red oxide of lead and charcoal is ignited in a crucible, a button of metallick lead will be found at the bottom of the vessel.

Pure water, has no direct action on lead; but it facilitates the

action of the air, for when lead is exposed to the air and kept constantly wet, it is oxidated much more rapidly than it otherwise would be. Hence the reason of the white crust which appears upon the sides of leaden vessels containing water, just at the place where the upper surface of the water terminates. This oxide is soluble to a certain extent in water and thus unpleasant symptoms may accrue from keeping this fluid intended for drinking in cisterns lined with lead.

Water appears also to act more readily on lead, when impregnated with the neutral salts that are occasionally contained in spring water. This fact cannot be better illustrated, than by referring to the account given by Dr Wall (in a letter to Sir George Baker) of a family residing in the town of Worcester. "A gentleman" (he says) "of this town was the father of a numerous offspring "having had one and twenty children, of whom eight died young "and thirteen survived their parents. During their infancy, and "indeed untill they had quitted the place of their usual residence, they were all remarkably unhealthy; being particularly "subject to disorders of the stomach and bowels. The father

"during many years was paralytic. The mother for a long time
"subject to cholicks and bilious obstructions. She died at last of an
"obstinate jaundice. This disease had been several times removed
"by the use of Bath water but it always came on again soon
"after her return to Worcester; and at last eluded every method
"and medicine which was tried.

"After the death of the parents, the family sold the house
"which they had so long inhabited. The purchaser found it
"necessary to repair the pump. This was made of lead which
"upon examination, was found to be so corroded that several
"perforations were observed in the cylinder in which the bucket
"plays; and the cistern in the upper part was reduced to the
"thinness of common brown paper and was full of holes like a sieve.
"The waters of the town are remarkably hard, so much so as to
"curdle soap, coagulate milk, and let fall a copious precipitate
"on the addition of an alkali either fixed or volatile, and in dry
"seasons its taste is bitter and aluminose. This water
"evidently contained an acid property, which enabled it to act
"upon and render soluble a considerable portion of the lead".—

Sulphuric acid has no direct action on lead except when concentrated, and at a boiling temperature. It is then decomposed, and sulphurous acid is formed. The insolubility of lead in sulphuric acid, occasions its being employed as the material for constructing the chambers in which that acid is prepared, and even for boiling down the weak acid. Sulphate of lead however may be formed either by adding sulphuric acid, or what is still better sulphate of soda to any of the salts of lead. Its insolubility renders its formation of use as a step in mineral analysis and hence it is necessary to know its exact composition: which is stated by Berzelius, as follows,

Sulphuric acid	26.34	100
Yellow oxide	73.66	279
		379

Nitric acid acts upon lead with considerable energy provided it be not too much concentrated; first converting it into a white powder, which is a sub nitrate; and then dissolving it especially when assisted by heat. The yellow oxide of lead is dissolved by nitric acid completely, and without effervescence; but the red oxide is rendered white and a portion as I have

before nitric is, is diſsolved leaving a precipitate converted into the brown oxide. —

The nitrate of lead is always formed when lead is diſsolved in nitric acid, unleſs there be present an exceſs of lead, and a strong heat be applied; it is formed also by diſsolving the carbonate or white lead in nitric acid. The solution is transparent and colourleſs and when sufficiently concentrated by evaporation, crystallizes on cooling. The crystals are usually tetrahedrons, having their apex truncated. They are opaque and white and have a silvery lustre; soluable in 7½ parts of boiling water; they contain no water of crystallization, and consist according to Berzelius of —

Nitric acid	32.78	100.
Yellow oxide	67.22	209.5

Chevreul considers this salt a super nitrate and describes a pearl coloured scaly salt, which is supposed to be the neutral nitrate consisting of;

Nitric acid	19.86	100.
Yellow oxide	80.14	403.

Nitrite of lead according to Thomson was discovered by Proust; but its true composition was first ascertained by Berzelius & Chevreul, and from their experiments he has stated; "it would "appear that there are three sub-species of this salt, the ni"trite subnitrite and quadrosubnitrite. The first composed of 1 atom of acid, + 1 atom base, the second 1 atom acid + 2 atoms base, and the third 1 atom acid + 4 atoms base.

When a solution of nitrate of lead is boiled upon lead in the metallick state, it forms a subnitrate of this metal; the lead is gradually dissolved, being oxydised at the expense of the acid which partly flies off in the state of nitrous gas, and is partly converted into nitrous acid. If the requisite portion of lead only is dissolved, which according to the experiments of Berzelius amounts to 7.8 parts of lead for every ten parts of nitrate of lead employed, the solution has a yellow colour and deposits subnitrite of lead in scales: but if a greater quantity of lead has been dissolved quadrosubnitrite is likewise formed, and almost the whole is converted into this salt, when as much lead as possible is dissolved, by boiling on it a solution of nitrate of lead.

The nitrite crystallizes in red plates, is sparingly soluble in cold water and boiling water dissolves only about a tenth of its weight. It was composed, according to Chevreul by all experiments that were tried. Its constituents are

Nitrous acid	18.15	100
yellow oxide	81.85	450

The sub-nitrite crystallizes in needles of which 100 parts of boiling water, dissolve about three parts and retains about one when cooled down to 73° of Fahrenheit It consists of

Nitrous acid	9.9	100.
yellow oxide	90.1	910

When the nitrate, or any other soluble salt of lead is added to a solution of common salt, a precipitate takes place of muriate of lead. The same compound may be formed, by introducing heated lead into chlorine gas; it does not burn but absorbs the gas, and is converted into a chloride of lead. It may also be obtained by treating the oxides of lead with muriatic acid. When dry the compound is a dull semi transparent substance; fusible at a heat below redness. and volatile at an

intense heat. It has a sweet taste and is soluble in 22 parts of cold water. It has received the names of horn lead, muriat of lead, and plumbane; Berzelius states its composition to be

muriatic acid	19.64	100.
yellow oxide	80.36	409.00

According to Sir H. Davy, it is composed of chlorine with metallic lead, or chloride of lead, composed of —

Chlorine	24.62	100
Lead	75.38	306

The sub-chloride of lead called mineral or patent yellow, is made by mixing two parts of the red oxide of lead, with one of muriat of soda: this mixture is made into a paste with water; the common salt is decomposed and a muriat or probably sub-muriate of lead is formed; which on fusion affords this substance. The soda is disengaged and attracts carbonic acid from the atmosphere, but not enough to convert it into a carbonate. —

A compound of lead with phosphorus may be formed by fusing together equal parts of filings of lead and phosphoric acid.

It is of a silver colour with a shade of blue may be cut with a knife, but is brittle under the hammer.—

The same substance may be formed by bringing phosphorus in contact with melted lead. According to Pelletier, it consists of 88 parts of lead and 12 of phosphorus.

Having proceeded thus far in my account of the preparations of lead, I shall now mention a combination which though manufactured in quantities much greater than the others is almost exclusively applied to purposes appertaining to the arts, being seldom if ever (at present) resorted to as a medicinal article in the practice of medicine; though it may be employed in the formation of combinations exceedingly serviceable both to the Physician and Surgeon it is the

Plumbi Sub-carbonas vulgo Cerussa or White Lead.

The composition of this substance has not until lately been well understood, and hence arose a diversity of appellations; but to Bergman the credit has been attributed of having discovered it to be a carbonated oxide of lead and not an acetite, or sub-acetite though the acetous acid is the

means of its formation, by acting upon the metal and thus producing an oxide with which oxide the carbonic acid generated by the decomposing vegetable matter (in which the lead is placed) gradually unites, until the whole is thus formed into a sub-carbonate.

It is also probable (as has been suggested to me by my Brother Mr John P Wetherill) that as the acetic acid is decomposed; the portion of carbon which it contained, may be afforded to the oxide, tending greatly to accelerate the process...

But as the plan adopted for the manufacture of ceruse in this country, differs in some respects from that recommended by authors and pursued in Europe, I feel myself obliged to dwell more particularly and enter more fully into the peculiar mode pursued for its preparation.

Lead is melted and cast so as to form a sheet about two feet and a half long and five or six inches in breadth, being from $1/40$ to $1/60$ of an inch in thickness. The lead in this instance is cast at once of the proper form and not mechanically flattened as sheet lead usually is. By this plan the texture of the metal is rendered more open and more

easily penetrated by the acid vapour. These plates are then rolled up into loose coils and each is placed perpendicularly in an earthen pot, peculiarly formed, only large enough merely to contain the coil and having on its inner surface projections which prevent its coming in contact with the bottom of the pot; and which projections also answer the purpose of allowing a considerable portion of vinegar (which is to be placed in them) to be contained, without wetting the lower part of the lead.

These pots are then ranged in beds, (as they are called) under a building that shelters them from the weather, layer upon layer, being covered with boards and having intervening between each layer, fresh stable litter*

The heat of the dung acting upon the vinegar causes it to evaporate, and the lead kept constantly in contact with the acid vapour but not immersed in the liquor, soon begins to corrode or oxidate. The pots remain under the litter for about six weeks or two months at the end of which time they are taken out and the coils are

brittle sub-carbonate -.

But as the action throughout the whole bed is not equable there are generally some small portions of the metal which have not been acted upon by the acetous acid and thus escaped corrosion; these are to be carefully separated by means of a sieve. —

This sub-carbonate, is mixed with water and passed between a pair of mill stones; the finer parts are separated from the a coarser by successive washings, or rather by letting the water in which this preparation is suspended flow through cisterns, the fine particles pass off, whilst those which by grinding have not been rendered sufficiently so deposit in the first cistern and are again ground — The finer part being more readily suspended in water is deposited in the last cistern; this is to be well levigated and after the ceruse has, precipitated, a sufficiency of the water is drawn off to render it fit for drying; it is then placed upon kilns and by a gradual fire all water is evaporated from it; when this is effected it then constitutes ceruse or the white lead of commerce. —

As I have in the preceding pages, made particular mention

of the red, yellow, and puce coloured oxides of lead, (which have usually been mentioned by authors in this piece) I shall continue my subject by calling the attention of my readers to a preparation entitled,

Plumbi Oxydum Semivitreum or Litharge.—

This preparation, according to Thomson is the yellow oxide combined with four per cent of carbonic acid; to form it, maſsicot is usually thrown into a furnace; the heat being increased suddenly and to a great degree, it melts and has somewhat the appearance and consistency of oil and on cooling, concretes into this substance, the carbonic acid being derived from the carbonaceous matter burnt in the flame of the furnace. Litharge is also formed during the extrication of silver from lead. Its colour is yellow, varying in degree according to the heat of the fire to which it has been exposed.—

The uses for which it has been employed in Pharmacy are for making plasters as the Emplast: Plumbi, and Ceratum Saponis. It is also used for the formation of Goulards extract.

Litharge ~~This~~ (as well as other preparations of lead) is sometimes fraudulently

added to cyder or the inferior french wines, to remove or prevent acidity. This deliterous adulteration may be detected (as may all other solutions of lead) by sulphuretted hydrogen water, which will throw down the lead in the state of a dark brown sulphuret.

The sesqui-carbonate of ammonia, which is a more delicate test may be employed to precipitate the lead in the form of a white carbonate, which on being washed and digested with sulphuretted hydrogen water, will instantly become black: this heated on charcoal before the blow pipe, will yield a globule of lead.

Chromate of potash will also throw down from all saturnine solutions a beautiful orange yellow powder.

Ferrocynate of potash occasions a white precipitate, as also does gallic acid and infusion of nut galls.—

A plate of zinc kept in a solution of lead occasions either a white precipitate, or the lead appears in its metallic state.

Saturnine adulteration may however be more positively ascertained by evaporating the suspected liquor to a thick fluid, add charcoal and calcine in a crucible: in the space of an hour

metallick points will be obtained, consisting of lead surrounded by a quantity of yellow oxide. —

I will continue my account by mentioning another preparation of lead which though of use in the arts, is considered as a remedial article to be of greater utility to the Physician than any of those heretofore spoken of, I allude to the

Plumbi Acetas. Super Acetate of Lead. Saccharum Saturni
vulgo Sugar of Lead.

The recipe recommended in our dispensatories for the preparation of this article is to take of

"Sub-carbonate of lead - - - - - - - any quantity
"Purified Vinegar ten times its weight
"Digest these in a glaſs veſsel untill the vinegar becomes sweet, "having poured this off add more vinegar untill it ceases to "become sweet. Filter the liquor and crystallize by alternate "slow evaporation and refrigeration. The crystals are to be dried "in the shade. —

But the proceſs for forming this article as I have seen it pursued differs from the foregoing and is attended with much

be taken; the quality of the preparation when formed being equally good.

Instead of using the subcarbonate of lead as recommended; manufacturers have found it preferable to use the metal itself, which is prepared for the purpose by being poured whilst in a melted state into water; this forms it into detached pieces of a loose texture, these pieces are then collected and placed in tubs. Purified vinegar is poured upon them and suffered to remain for sometime, untill it has acquired a sweet taste; it is then drawn off and after evaporating untill it has acquired a sufficient consistency is suffered to crystallize.. This process by adding fresh vinegar may be continued, untill the whole of the lead in the tubs is taken up by acetic acid.—

Most of the sugar of lead used in England is imported from Holland. In that country it is formed very nearly in the manner of ceruse, that is, sheets of lead are put in pots with vinegar and digested a sufficient time, but here the vinegar is distilled and the plates instead of being entirely

out of the liquor are half immersed in it. This being done the upper half is soon covered with an efflorescence of ceruse, after which it is immersed in the vinegar and the part which was before immersed is now brought up to be converted into ceruse as before, when the plate is again turned, and the newly oxidated surface in its turn buried in the liquor.

When prepared by either of the methods which I have considered, it consists of irregular masses resembling lumps of white sugar; being an aggregation of acicular four sided prisms terminated by dihedral summits, which are slightly efflorescent. This salt has an astringent sweetish taste; the specific gravity is 2.34 and without an excess of acid it will not be rendered soluble in less than 25 parts of water; when dissolved in water a white powder is deposited, which is a carbonate of lead formed by the carbonic acid contained in the water; and the same salt is thrown down by blowing a current of air from the lungs into the solution.

When dry acetate of lead is briskly heated without addition in a retort, it gives out an acetous ~~acid~~ foetid liquor, and

the residue of the distillation furnishes a good pyrophorus. But Proust in distilling it very slowly obtained first a watery vinegar, then a yellow liquid with the smell of alcohol but rather empyreumatic, from which when saturated with potash a strong smelling aethereal oil separated. The liquid distilled from the solution furnished a strong inflammable fluid resembling ether. —

To continue my account of the preparations of lead I will mention a combination of litharge and strong vinegar introduced into practice many years ago by a French surgeon of Montpelier named Goulard, which he called Extract of saturn but which since his time has acquired different appellations, as, Goulard's extract. Aqua Lithargyri Acetati and Extract of lead.

To obtain this preparation, it is necessary to take of the ingredients, in the proportions of—

Litharge - - - - - one pound
Strong vinegar - - - - - - - two pints

Put them together into a glazed earthen ware pipkin

and let them boil or rather simmer, for an hour or an hour and a quarter, taking care to stir them all the while with a wooden spatula. After the whole has stood to settle pour off the clear liquor which is upon the top for use. ——

This is Goulard's original preparation it is of a straw colour with a slight admixture of green and has the specific gravity of 1.22. One hundred drops of this with four teaspoonsfull of brandy mixed with a quart of water form his famous vegeto mineral water.

Dr Coxe in his dispensatory mentions this preparation (on the authority of Dr Bostock) as differing from acetate of lead only in the different proportions of the same ingredients; "thus" (says he) "in the saturated solution of "the sugar of lead and the water of acetated litharge; it "appears the constituents are respectively

	acetate	Goulard
"Oxyd of lead	16.8	23.1
"Acetic Acid	7.5	5.
"Water	75.7	71.9

The author just quoted has also mentioned that "Thenard
"obtained the salt in crystallized plates by boiling 150 parts
"of litharge in a solution of 100 parts of sugar of lead; and
"on analysing it found it to consist of 17 and 78 oxyd and
"5 water. These experiments, the coincidence, of which
"confirms their accuracy, since that in sugar of lead 100
"parts of acid are combined with 224 parts of oxyd of lead,
"and in goulards extract with 450 or 460 or somewhat more
"than twice the quantity of oxyd. —
"Now according to the doctrine of definite proportions,
"any acid always combines with the same proportion of oxygen
"in oxyds, whatever the proportion of metal may be: it is
"therefore evident that the oxygen in the oxyde of lead,
"contained in goulards extract, is combined with twice as
"much lead as it is in the oxyd of the sugar of lead; or
"goulards extract is the *acetate* of the peroxide of lead.

Another preparation formed from that just mentioned
which is the last I shall consider, is the
Liquor Subacetas Lythargyri compositus. Compound Liquor

of acetated litharge: to form it you take of—

Liquor of acetated litharge	a drachm
Distilled water	fourteen ounces
Weaker spt of wine	a drachm

Mix the spirit and liquor of acetated litharge then add the distilled water.—

Finis